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THEORETICAL STUDIES OF IMPORTANT PROCESSES IN  
PLANETARY AND COMET ATMOSPHERES

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## I. The Calculation of Dissociative Recombination Cross Sections and Rates

The dissociative recombination (DR) of the  $AB^+$  molecular ion with an electron is described by:



where the product atoms may be electronically excited and the  $AB^+$  ion may be vibrationally excited. Dissociative recombination of molecular ions has been shown to be an important component in the detailed interpretation of planetary ionosphere data returned by many NASA missions ranging from the early Mariner and Viking missions to Pioneer Venus and Voyagers I and II. Indeed, knowledge of the details of DR will be needed for the interpretation of data from many future missions. Unfortunately, several aspects of reaction (1) make it exceedingly difficult to study in the laboratory. These include the difficulty of generating the  $AB^+$  ions in specified vibrational distributions which match those found in planetary atmospheres and the difficulty of identifying the electronic states of the products. In order to circumvent these difficulties we have developed a first principles theoretical approach for calculating the DR cross sections and rates. Our calculations have focused on  $O_2^+$  DR and are the first calculations to include the indirect DR mechanism (discussed below) for a molecule larger than  $H_2^+$ . Below we discuss our progress in the calculation of DR cross sections and rates.

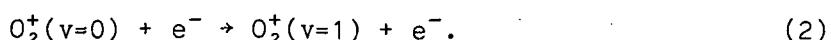
There are two fundamental mechanisms driving DR. In direct DR,<sup>1</sup> the electron is captured into a repulsive state of the neutral molecule followed by dissociation to neutral products. In indirect DR,<sup>2</sup> electron capture can also occur into a vibrationally excited Rydberg state which can either autoionize or dissociate along the repulsive state of the direct DR mechanism. These excited Rydberg levels can have the ground state of the ion or an excited electronic state as the electronic core. These neutral levels are resonances since they exist in the electron-ion continuum of the ion ground state. In practice, both the direct and

indirect mechanisms occur simultaneously and interfere with each other. We have used Multichannel Quantum Defect Theory and have developed an approach<sup>3</sup> which describes both mechanisms simultaneously yielding complicated resonance structures in the cross section. Prior to our work, the interaction which drives the indirect mechanism was assumed to be primarily vibronic. In the vibronic mechanism the electron is captured by interacting directly with the nuclear motion so as to excite the molecular ion from the initial vibrational level to an excited vibrational level of a Rydberg state. This mechanism involves a breakdown of the Born-Oppenheimer approximation in which the nuclear and electronic motion are taken to be separate and noninteracting. It can be shown that the vibronic coupling is primarily important for transitions in which the vibrational quantum number of the ion and the neutral Rydberg state differ by unity. In practice this restricts the Rydberg levels to principal quantum numbers of about  $n=7,8$ . However, we have found that there is also a second order electronic mechanism which also drives capture into the Rydberg states. In the electronic mechanism, each Rydberg vibrational level is electronically coupled to the repulsive states of the same electronic symmetry. Because of this coupling, capture into the repulsive state can also populate the Rydberg levels. In this higher order electronic coupling, the electron is first captured into the repulsive state followed by transfer to the Rydberg state followed finally by transfer back to the dissociative state. Dissociation then completes this DR mechanism. In addition, the transition is not restricted to  $\Delta v=1$ . Indeed, the couplings are large for Rydberg levels with low principal quantum number ( $n=3$ ) and high  $v$  ( $v=13$ ). The vibronic and electronic indirect mechanisms interfere with each other. Furthermore, interference also occurs between neighboring Rydberg levels. Thus in addition to interference with the direct mechanism a considerable amount of simultaneous interference is described, leading to a complicated resonance structure in the calculated cross sections.

An additional interesting feature of our calculation is the role played by Rydberg vibrational levels which lie below the  $v=0$  level of the ion. These levels might not ordinarily be considered to be

resonances since their centers lie below the electron-ion continuum. However, even though these states are discrete below the  $v=0$  level of the ion, they have wings which extend above the  $v=0$  level. Furthermore, these wings, which result from interfere with the direct mechanism, play an important role in determining the magnitude of threshold cross sections and rates. An example (see the attached reprint) is the  $n=3$ ,  $v=12$   $^1\Sigma_u^+$  Rydberg level of  $O_2$  found at 0.1eV below the  $v=0$  level of  $O_2^+$ . Because this level has a negative Fano profile index,  $q$ , it interferes with the direct mechanism so as to decrease the full DR cross section below that due to the direct mechanism. This level also causes the calculated full rate at low electron temperatures to be below the direct rate. The same phenomenon occurs in the  $v=1$  and  $v=2$  rates along the  $^1\Sigma_u^+$  channel where below threshold resonances reduce the full rate below the direct rate just above threshold.

We have also studied vibrational excitation cross sections and rates which describe the following reaction:



The same approach developed for the study of DR, described in detail in the attached reprint, can also be used to study vibrational excitation (VE).<sup>4</sup> In VE, the electron is emitted prior to dissociation and the molecule is left in an excited vibrational level. The repulsive states responsible for DR act as intermediate resonances in VE and greatly enhance the VE rate over the small value that would be expected in the absence of an intermediate state. Cross sections for vibrational excitation plotted as a function of electron energy show similar complex resonance structure as found for DR. In the case of  $v=0 \rightarrow 1$  excitation including only the  $^1\Sigma_u^+$  dissociative route of  $O_2$ , we found a rate of  $1.7 \times 10^{-11} \text{ cm}^3/\text{sec}$  at 800K. While this rate is small, it accounts for only the  $^1\Sigma_u^+$  intermediate state. There are a number of other channels having more favorable intersections with the ion and these channels are being explored in current work. Vibrational deexcitation is also being studied.

## II. The Calculation of Electron Capture Widths

An important quantity needed for the calculation of cross sections and rates is the electron capture width. These have now been calculated for all the states of  $O_2$  that are of importance to dissociative recombination of the lowest 10 vibrational levels of the ion. The approach, described in more detail in prior progress reports, uses a basis set of 18 diffuse Gaussian functions<sup>5</sup> centered at the molecular midpoint. Rydberg orbitals coupled to the ground state of  $O_2^+$  are determined in Improved Virtual Orbital calculations. For each total electronic symmetry an optimized set of Rydberg orbitals is generated. The width is calculated using valence configuration interaction wave functions for both the dissociative state and the Rydberg states. High non-physical routes in the dissociative wave function CI are allowed to provide correlation to the Rydberg CI wave functions. With this procedure we are able to calculate accurate widths up to principal quantum numbers of about 13 where the width has converged to the limiting value ( $n=\infty$ ). A tabulation of the calculated widths for all the important  $O_2$  DR routes is given below in Table 1.

The largest widths calculated for  $O_2$  are for the  $1^1, 3\Pi_u$  states. These states are shape resonances since they correspond mostly to an

State	$\Gamma$ (eV)	State	$\Gamma$ (eV)
$1^3\Pi_u$	1.5498	$4^1\Pi_g$	0.0000
$2^3\Pi_u$	0.0137	$b^1\Sigma_g^+$	0.6476
$3^3\Pi_u$	0.0131	$2^1\Sigma_g^+$	0.0013
$1^1\Pi_u$	2.2302	$3^1\Sigma_g$	0.0051
$2^1\Pi_u$	0.0301	$a^1\Delta_g$	0.5595
$3^1\Pi_u$	0.0163	$2^1\Delta_g$	0.0083
$1^3\Pi_g$	0.0026	$1^1\Sigma_u^+$	0.2864
$2^3\Pi_g$	0.0001	$1^3\Sigma_u^+$	0.0042
$3^3\Pi_g$	0.0066	$2^3\Sigma_u^+$	0.0072
$4^3\Pi_g$	0.0003	$2^1\Sigma_u$	0.0164
$1^1\Pi_g$	0.0034	$1^1\Delta_u$	0.4377
$2^1\Pi_g$	0.0234	$X^3\Sigma_g^-$	0.4397
$3^1\Pi_g$	0.0014	$2^3\Sigma_g$	0.0319
$1^3\Sigma_u$	0.9065	$3^3\Sigma_g$	0.0000
$2^3\Sigma_u$	0.0016	$1^3\Delta_u$	0.0393
$1^1\Sigma_u$	0.2060	$2^3\Delta_u$	0.0077

Table 1. Calculated electron capture widths for  $O_2$ .

electron being captured by the ion into a  $3\sigma_u$  orbital without any rearrangement of the other electrons. Using orbitals optimized for the  $1\Pi_u$  states we find that the  $n=7$  widths for  $1,2,3^3\Pi_u$  repulsive states are 1.55, 0.014, and 0.013eV respectively while the widths for  $1,2,3^1\Pi_u$  are 2.23, 0.030, and 0.016eV respectively. The upper two states have small capture widths because their configurations differ by a triple excitation from the ion plus a free electron. All widths in Table 1. are for a single internuclear distance,  $R=2.2819a_0$ , the equilibrium separation of the ground state. Table 1. allows us to reduce the possible routes that can lead to DR in  $O_2^+$  to a very small number of probable routes. The Table shows that the  $1^3\Pi_u$ ,  $1^1\Pi_u$ ,  $1^1\Sigma_u^-$ ,  $1^3\Sigma_u^-$ ,  $1^1\Sigma_u^+$ , and  $1^1\Delta_u$  states are the primary routes for DR of  $O_2^+$ . Note that while the X, a, and b states have significant calculated widths they are unlikely DR routes since their potential curves do not cross the ion curve. The Table shows that for symmetries having a large width, i.e.  $>0.1$ eV, the large width occurs in only a single root of that symmetry and always in the lowest root. We are currently studying other molecules, including OH and  $N_2$  in order to see if their electron capture widths show a similar variation.

### III. DR of $N_2^+$

We have recently completed calculations of the DR of  $N_2^+$ .<sup>6</sup> In order to obtain accurate results, these calculations employed configuration interaction (CI) wave functions having over one million terms. As in the study of  $O_2$ , we found that the cross section has a complex structure due to many interacting resonances. We also found that the indirect DR mechanism decreased the full DR rate below the rate due the direct mechanism. As in  $O_2$ , this effect is due to an important resonance lying below the  $v=0$  level of the ion. The calculated rate for electron temperatures ( $T_e$ ) between 100K and 1000K was found to be  $1.6 \times 10^{-7} \times (T_e/300)^{-3.7} \text{cm}^3/\text{sec}$  in excellent agreement in both magnitude and temperature dependence with prior microwave results.<sup>7</sup> The calculations also show that the primary DR channel is the  $C^3\Pi_u$  state which generates  $^4S$  and  $^2D$  nitrogen atoms having 1.72eV kinetic energy. This energy is sufficient for escape from the Martian atmosphere and DR

is a very important component of models of the N density and of the  $N^{14}/N^{15}$  isotope ratio. The latter quantity is affected because  $N^{15}$ , which needs 1.86eV to escape, will not be able to escape from DR of  $v=0$ . The net effect is isotope enhancement from DR of  $v=0$ .<sup>8</sup> A reprint giving more details is attached to this report.

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## V. Publications Acknowledging NASA Support

1. S. L. Guberman, Ab Initio Studies of Dissociative Recombination, in Dissociative Recombination: Theory, Experiment and Applications, ed. by J. B. A. Mitchell and S. L. Guberman (World Scientific, Singapore, 1989), p.45.
2. J.-H. Yee, S. L. Guberman, and A. Dalgarno, Collisional Quenching of  $O(^1D)$  by  $O(^3P)$ , *Planet. Space Sci.* 38, 647 (1990).
3. S. L. Guberman, Dissociative Recombination of the Ground State of  $N_2^+$ , *Geophys. Res. Lett.* 18, 1051 (1991). (See Appendix).
4. S. L. Guberman and A. Giusti-Suzor, The Generation of  $O(^1S)$  from the Dissociative Recombination of  $O_2^+$ , *J. Chem. Phys.* 95, 2602 (1991). (See Appendix).
5. S. L. Guberman and A. Dalgarno, Dipole Moments and Transition Probabilities of the  $i^3\Pi_g-b^3\Sigma_u^+$ ,  $c^3\Pi_u-a^3\Sigma_g^+$ , and  $i^3\Pi_g-c^3\Pi_u$  Systems of Molecular Hydrogen, *Phys. Rev. A.*, submitted for publication.
6. S. L. Guberman, The Calculation of Molecular Threshold Capture Widths, *J. Chem. Phys.*, to be submitted.
7. S. L. Guberman, The Dissociative Recombination of  $O_2^+$  Leading to  $O(^1D)$ . *J. Chem. Phys.*, to be submitted.

### Book

The author is co-editor with J. B. A. Mitchell of a volume entitled: *Dissociative Recombination: Theory, Experiment, and Applications*, published by World Scientific, Singapore, in 1989.

## VI. Appendix

1. S. L. Guberman and A. Giusti-Suzor, The Generation of  $O(^1S)$  from the Dissociative Recombination of  $O_2^+$ , *J. Chem. Phys.* 95, 2602 (1991).
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